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LASER RAMAN SPECTROSCOPY OF FLAMES:
THEORY AND PRELIMINARY RESULTS

J. A. Vanderhoff
R. A. Beyer

January 1981



US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) (clt) A Raman spectroscopy apparatus using intracavity argon ion laser excitation and photon counting detection has been used to measure both pure rotational and rotational-vibrational spectra of N ₂ from room temperature up to approximately 2200 K using pure gas samples, methane-air, and methane-nitrous oxide flames. Synthetic spectra generated by computer have been used to extract temperatures from the rotational-vibrational data using peak height ratios.		

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I. INTRODUCTION

The use of lasers to probe the combustion process has become a very active field of research. Due to the non-intrusive nature of light and the monochromaticity of the laser this tool is well suited to make detailed spatially and temporally resolved measurements in combustion environments. Raman scattering techniques (investigated here) can be applicable for probing the combustion process at elevated pressures since Raman scattering takes place in less than 10^{-12} sec, a time short with respect to other processes such as collisions.

We report here the use of spontaneous Raman techniques to measure the flame temperature of steady state flames. The $\text{CH}_4/\text{N}_2\text{O}$ flame was investigated most extensively in preparation for studies of the $\text{CH}_2\text{O}/\text{N}_2\text{O}$ flame. This latter flame is expected to be important in the flame zone of nitramine propellants since N_2O and CH_2O are major decomposition products^{1,2} of these propellants.

II. EXPERIMENTS

The experimental apparatus used for generating and detecting Raman signals is shown schematically on Figure 1. A 4 watt cw argon ion laser operating at 488 nm is used as the excitation source. This laser has its cavity extended to the mirror M (2.5% T, 5 m radius mirror) to allow both the focussing lenses L1 (100 mm focal length, AR coated) and the sample (slot burner) to be placed inside the laser cavity. This technique provides a significant increase in laser flux. Ideally one could obtain a factor of ~ 80 gain using the 2.5% transmitting mirror for the laser output coupler M. However slight losses from inserting the focussing lens and flame inside the cavity result in lower gains. The laser power is monitored by measuring the portion of the beam that is transmitted through M with a thermopile. The thermopile output is converted to digital data and recorded with a single counter denoted by SC.

Part of the light scattered from the flame is collected at right angles with a camera lens L2 (50 mm focal length, f1.0) and is focussed into a double monochromator DM by lens L3 (254 mm focal length, f5). Alignment of the collected light with the monochromator entrance slit is accomplished with a dove prism D. A (thermoelectrically cooled) RCA 31034 photomultiplier is used as the detector.

¹C. U. Morgan and R. A. Beyer, "ESR and IR Spectroscopic Studies of HMX and PDX Thermal Decomposition", 15th JANNAF Combustion Meeting Proceedings, CPIA Publication No. 297 (1978).

²B. B. Goshgarian, "The Thermal Decomposition of Cyclotrimethylene-trinitramine (RDX) and Cyclotetromethylenetetranitramine (HMX)", Report AFRPL-TR-78-76, Edwards AFB, CA (Oct 1978).

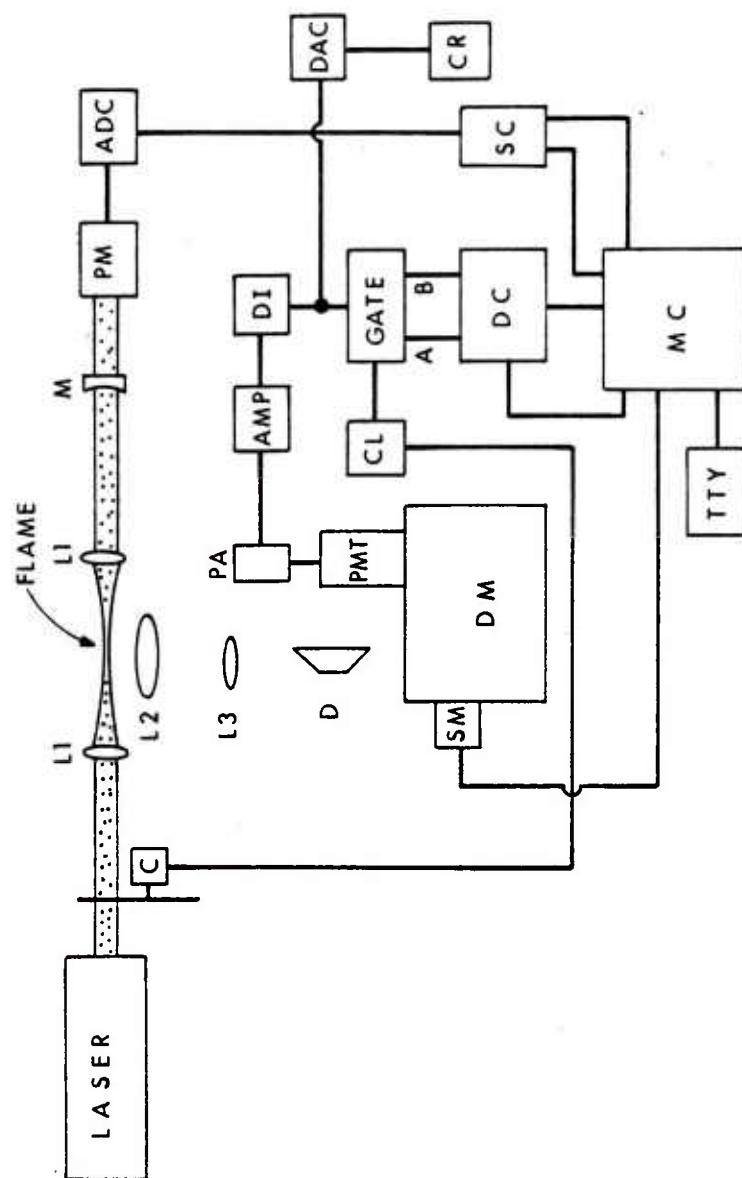


Figure 1. Schematic Diagram of Raman Apparatus

Two methods of recording the Raman signal are used. For recording a continuous spectrum the output from the discriminator goes through a digital to analog convertor (DAC) to a chart recorder where the time axis generally refers to scanning the wavelength at a fixed rate. When background emission from the flame is high another method which subtracts the signal with the laser off (B) from the signal with the laser on (A) is used. This is accomplished as follows. A chopper C is used to interrupt the laser beam and a trigger signal is sent to a clock CL. The clock opens the gate in the A or B position for equal amounts of time and the data is digitally accumulated with a dual counter, DC.

A microcomputer, MC, is used to control and collect data when operating in the gated mode. The amount of time desired to collect data at each wavelength together with the wavelength separation between data points are entered into the microcomputer. The microcomputer activates data collection for this period of time, then reads the data from the counters, computes A-B, corrects for possible laser power variations, and computes the statistical uncertainty in the data. These values are outputted to a teletype TTY. Next the microcomputer resets the counters and changes the wavelength of the DM by activating the stepper motor SM and the cycle is repeated.

Flames studied in this work were produced by a small, water-cooled slot burner constructed from copper. The slot dimensions are 0.33 mm wide and 28 mm long. Flow of the fuel and oxidizer to the burner were individually controlled by rotary flowmeters. In the results reported for the slot burner measurements were taken ~ 2 mm above the burner head. The spatial resolution of the sampled signal was a cylindrical element 65 μ m in diameter and ~ 1 mm in length.

III. THEORY

The Raman effect is a light scattering phenomenon whereby photons of light scattering from molecules have their energy changed. If the molecule gains energy it is termed Stokes scattering and anti-Stokes scattering if the molecule loses energy. The energy changes which occur are quantized according to the allowable energy levels (rotational and vibrational) of the molecule.

The selection rules for the change of vibrational (v) and rotational (J) quantum numbers for Raman scattering from diatomic molecules are^{3,4}

$$\Delta v = \pm 1 \text{ and } \Delta J = 0, \pm 2 . \quad (1)$$

³G. Herzberg, *Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules*, Van Nostrand, 2nd Edition, New York, 1950.

⁴S. Lederman, "The Use of Laser Raman Diagnostics in Flow Fields and Combustion", *Prog. Energy Combust. Sci.* 3, 1-34 (1977).

If one visualizes the Raman scattering process as an absorption-to and emission-from a virtual state then the process can be illustrated as shown on Figure 2.

A. Rotational Raman Scattering

Using a rigid rotor model for a diatomic molecule the rotational energy eigen values are

$$E_{\text{rot}} = \frac{h^2 J(J+1)}{8\pi^2 I} \quad , \quad (2)$$

where h is Planck's constant and I is the moment of inertia of the molecule. This equation is usually rewritten as

$$\frac{E_{\text{rot}}}{hc} = F(J) = BJ(J+1) \quad (3)$$

where $B = \frac{h}{8\pi^2 c I}$ is called the rotational constant and $F(J)$ is called the rotational term value. Using the selection rule $\Delta J = \pm 2$ the frequency separations ($\Delta\nu$) of rotational energy levels are

$$\Delta\nu = F(J+2) - F(J) = 4B(J+3/2). \quad (4)$$

This represents a series of Raman rotational lines on both sides of the Rayleigh line.

A rotational temperature can be calculated from determining the rotational quantum number J which has maximum intensity. The number of molecules N_J in rotational level J of a ground vibrational state at temperature T is

$$N_J = (2J+1) e^{-BJ(J+1)hc/KT}. \quad (5)$$

$$J_{\text{max}} \text{ occurs when } \frac{\partial N_J}{\partial J} = 0,$$

which gives

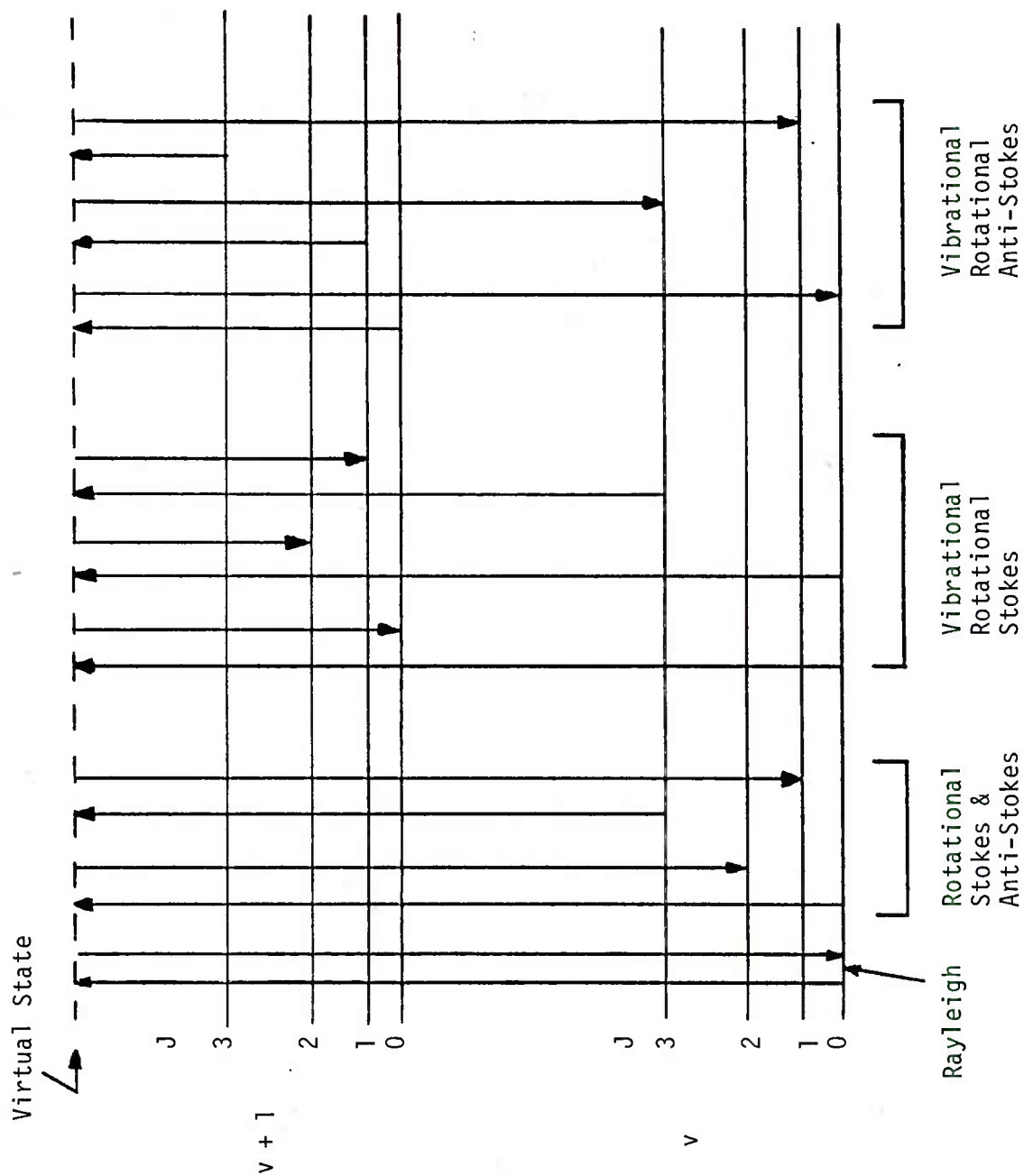


Figure 2. Representative allowed scattering processes for a diatomic molecule, including Rayleigh (elastic) and Raman (inelastic) processes.

$$T = (2J_{\max} + 1)^2 \frac{hcB}{2K} . \quad (6)$$

For rigid diatomic molecules the intensity of the Raman rotational lines in photons/s is³⁻⁵

$$I(J_i, J_f) = \frac{A_R g_n \nu^3}{Q_R} S(J_i, J_f) \exp [-BJ_i(J_i+1) hc/KT], \quad (7)$$

where J_i and J_f refer to the initial and final rotational quantum numbers, A_R is a collection of constants, and Q_R is the rotational partition function ($\approx KT/hcB$). The light frequency of Raman scattered light is $\nu = \nu_0 \pm 4B(J+3/2)$, where ν_0 is the frequency of the excitation source. The \pm appears in order to include both Stokes and anti-Stokes lines. $S(J_i, J_f)$ is the Raman line strength which is given as

$$S(J_i, J_{i+2}) = \frac{3(J_i+1)(J_i+2)}{2(2J_i+3)} \quad (8)$$

for the Stokes case and

$$S(J_i, J_{i-2}) = \frac{3J_i(J_i-1)}{2(2J_i-1)} \quad (9)$$

for the anti-Stokes case. The nuclear spin degeneracy factor g_n is responsible for the even-numbered J rotational lines to be missing for O_2 ; for N_2 the even J levels are twice as intense as the odd levels.

Rotational temperatures are commonly obtained from rearrangement of equation (7) as

$$F_o(J_i) \frac{hc}{KT} = \ln \left[\frac{I(J_i, J_f) C_1(\nu)}{S(J_i, J_f) g_n \nu^3} \right] + \text{const.} \quad (10)$$

⁵Michael C. Drake and Gerda M. Rosenblatt, "Rotational Raman Scattering from Premixed and Diffusion Flames", *Combustion and Flame*, 33 179-196 (1978).

and plotting such that hc/KT is the slope of a semi-log plot. $C_1(\nu)$ is the calibrated relative intensity response for the experimental detection system.

The effects of centrifugal distortion (i.e., a non-rigid rotor) and contributions due to rotational Raman scattering from vibrationally excited molecules have not been included.

B. Rotational-Vibrational Raman Scattering

In this section only the Q branch ($\Delta J=0, \Delta v=+1$) rotational-vibrational (ro-vib) spectra are considered for a diatomic molecule including contributions from harmonic and anharmonic oscillator terms, rigid rotor terms, and ro-vib interaction terms. The individual ro-vib Raman line positions are given by

$$\nu = \nu_0 \pm [T(v+1, J) - T(v, J)]. \quad (11)$$

$H(v, J)$ is the ro-vib term value which is

$$H(v, J) \approx W_e(v+1/2) - W_e X_e(v+1/2)^2 + W_e Y_e(v+1/2)^3 + [B - \alpha_e(v+1/2)]J(J+1). \quad (12)$$

W_e is the equilibrium vibrational frequency, $W_e X_e$ and $W_e Y_e$ are the anharmonic terms, and B and α_e are rotational constants. Using equation (12) in equation (11) we have

$$\nu = \nu_0 \pm [W_e - 2W_e X_e(v+1) + W_e Y_e(3v^2 + 6v + 13/4) - \alpha_e J(J+1)] \quad (13)$$

The individual line intensities are given by

$$I(v, J) \propto \frac{g_n(2J+1)(v+1)}{Q_R Q_v} \nu^4 C \exp \left[- \frac{hc}{KT} (H(v, J)) \right] \quad (14)$$

where C is a constant and Q_v is the vibrational partition function

$$Q_v \approx \frac{1}{1 - \exp \left[- \frac{hc}{KT} (W_e - W_e X_e + .75 W_e Y_e) \right]}$$

For a comparison of experimental data with equation (14) a computer program was generated to produce Q branch ro-vib Stokes Raman spectra for N₂ (see the Appendix).

IV. RESULTS

One of the first gas phase pure rotational Raman spectra that was recorded was obtained using a cell filled with 100 torr (1.33×10^4 pascals) of molecular oxygen. The results are shown on Figure 3. This spectrum is the anti-Stokes part where the peaks are labelled by the J rotational state. For oxygen only odd number J transitions appear due to nuclear spin degeneracy. The intensity of this rotational spectrum is maximum around J=9 from which an equilibrium rotational temperature can be computed. Using equation (6) with $B = 1.4456 \text{ cm}^{-1}$ a value of $T = 375^\circ\text{K}$ is obtained. The actual room temperature of the cell was 296°K . This technique is not very precise for low temperature especially using a molecule that has alternate J rotational levels missing. However it can be useful for obtaining approximate temperatures with a minimum of calculation.

To illustrate another method of obtaining a rotational temperature a rotational anti-Stokes Raman spectrum of room air was recorded and is shown on Figure 4. Here the predominant peaks come from rotational transitions in O₂ and N₂. Only the rotational levels for N₂ separated from the O₂ levels are used in the determination of the temperature. These levels are labelled on the figure. Using these intensities in equation (10) a temperature is obtained from the slope of a plot of

$$\ln \frac{I(J_i, J_f) C_1(v) 2(2J_i - 1)}{3J_i(J_i - 1) g v^3}$$

versus $F_0(J_i)$. This plot is shown on Figure 5. An unweighted least squares fit to the data gives a temperature of $294 \pm 15^\circ\text{K}$.

This method has been used to measure rotational temperature from flames produced on a slot burner operating at atmospheric pressure. An anti-Stokes rotational Raman spectrum of a rich CH₄-air flame was recorded at a position $\sim 2 \text{ mm}$ above the flame reaction zone. Using the N₂ rotational intensities in equation (10) a rotational temperature of $T = 1230 \pm 90^\circ\text{K}$ is obtained from a least squares fit to the data shown on Figure 5.

A higher temperature-flame was produced by using a near-stoichiometric CH₄/N₂O mixture. The anti-Stokes rotational Raman spectrum sampled again $\sim 2 \text{ mm}$ above the reaction zone is displayed on Figure 6 where the N₂ peaks used to calculate the rotational temperature are

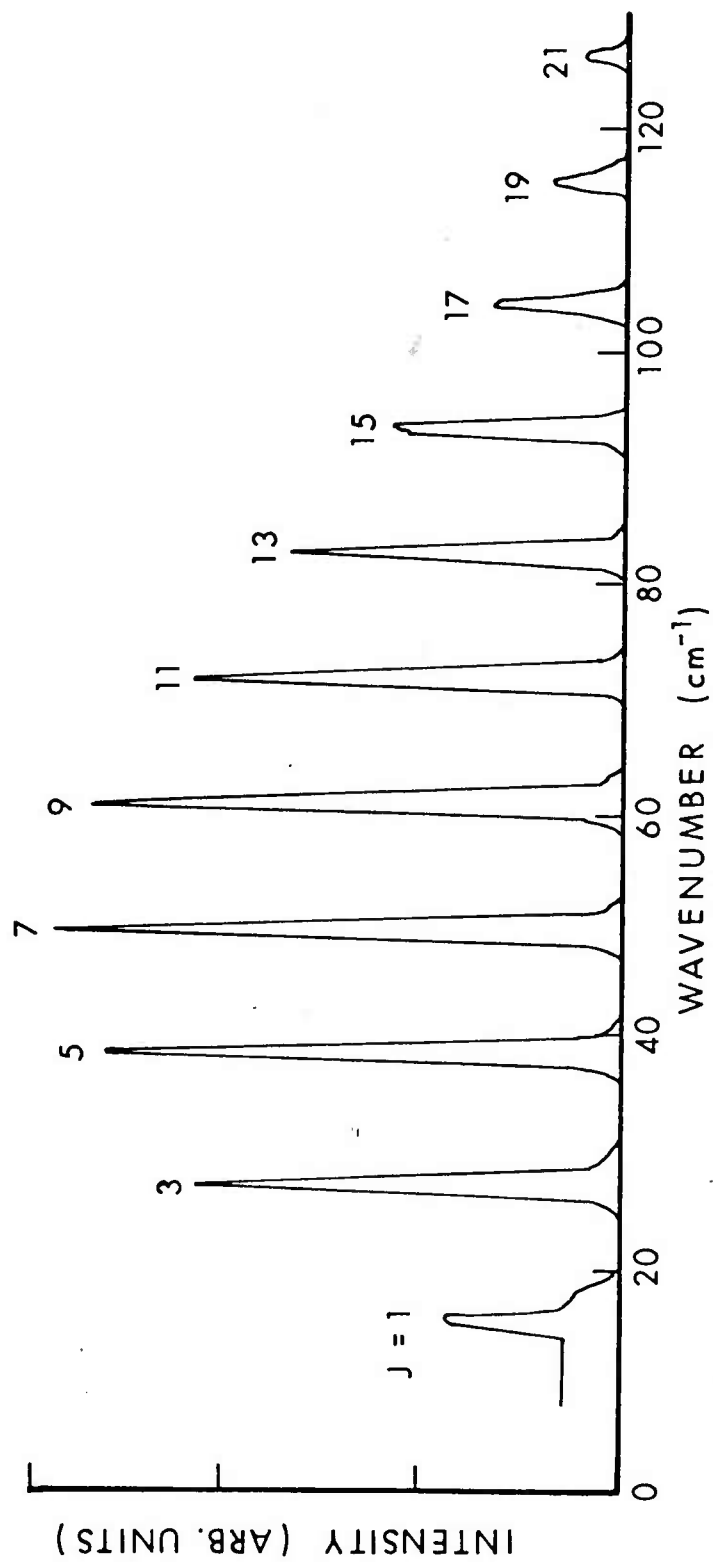


Figure 3. Rotational anti-Stokes Raman spectrum of 100 torr of oxygen at room temperature.

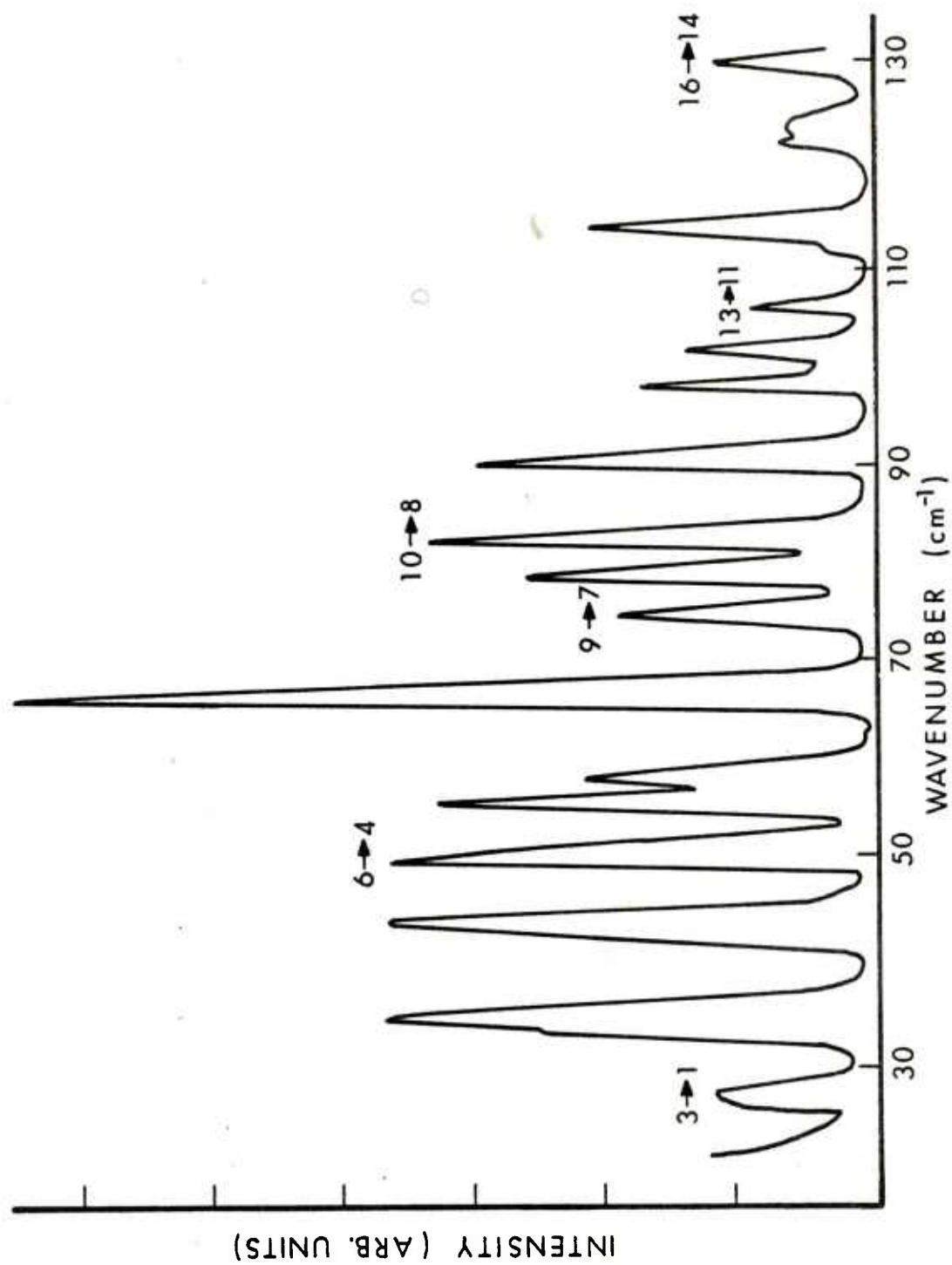


Figure 4. Rotational anti-Stokes Raman spectrum of room air

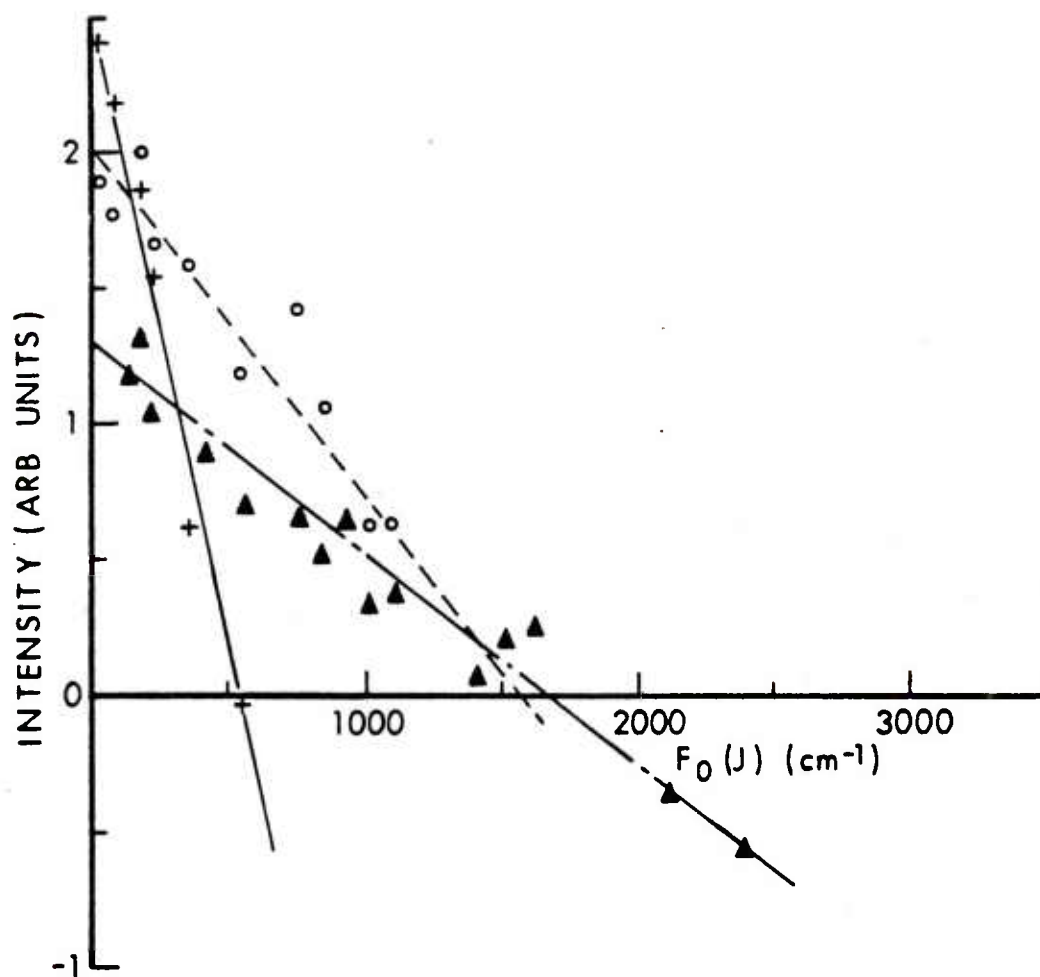


Figure 5. Boltzmann plot for N₂ from rotational Raman spectra recorded in room air (+), in a rich methane-air flame (o), and in a near stoichiometric methane-nitrous oxide flame (Δ).

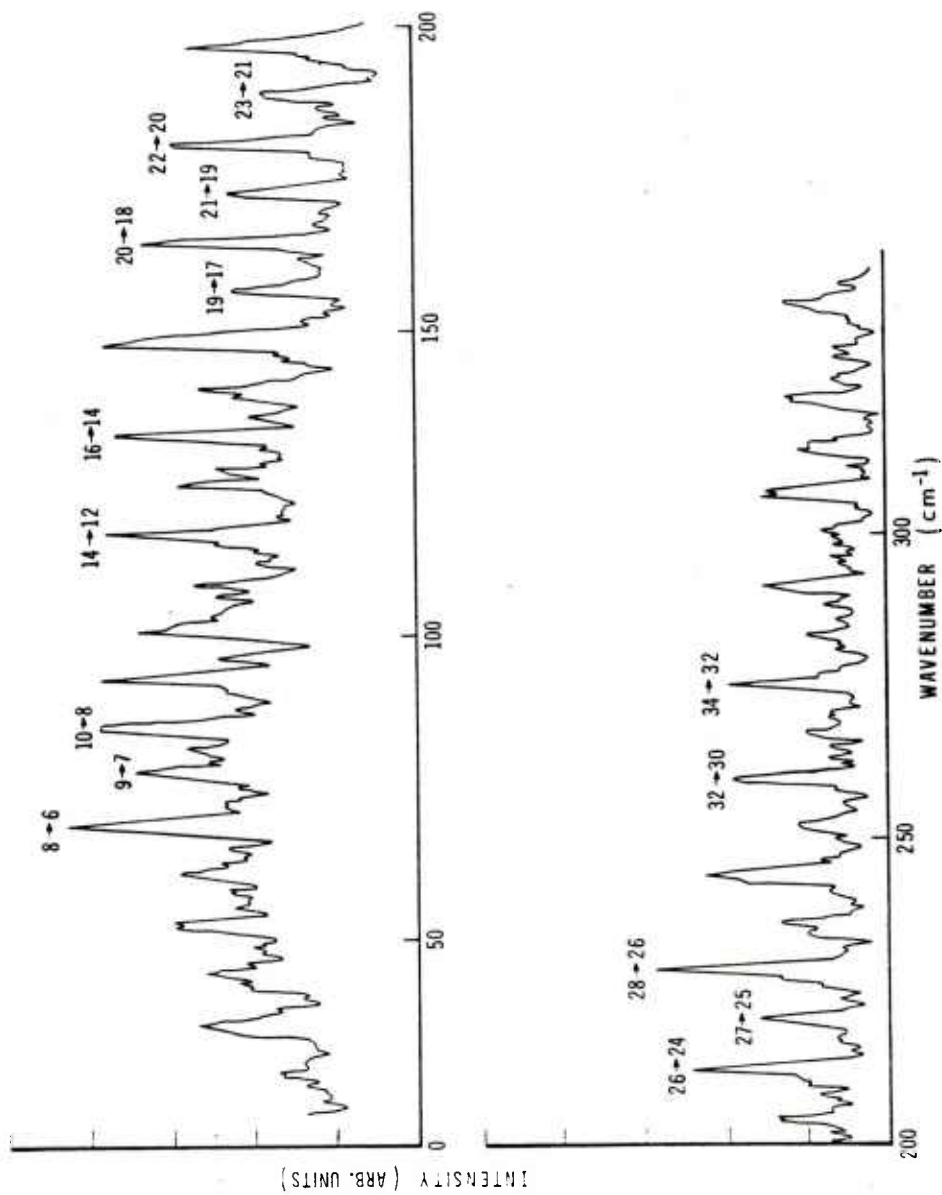


Figure 6. Rotational anti-Stokes Raman spectrum in a near stoichiometric methane-nitrous oxide flame. Nitrogen transitions used in temperature calculations are identified.

labelled. An underlying broad-smooth peak extending out to $\sim 200 \text{ cm}^{-1}$ is believed due to the rotational spectrum of CO_2 . At the higher rotational J values, peaks associated with the rotational spectrum of vibrationally excited N_2 start to appear out from under the ground vibrational state rotational peaks. The intensities obtained from this spectrum are again cast in the form of equation (10) and plotted on Figure 5. A rotational temperature of $1830 \pm 175^\circ\text{K}$ is obtained from a least squares fit.

At elevated temperatures excited vibrational states become sufficiently populated so that vibrational temperatures can be obtained from a comparison of the relative intensities. The cross section for vibrational Raman scattering is not as large as that of rotational scattering, but it is usually free from spectral interference of other molecular species. Figures 7, 8, and 9 show Stokes Q branch Raman ro-vib spectra for N_2 using a rich CH_4/air flame, a near stoichiometric CH_4/air flame, and a near stoichiometric $\text{CH}_4/\text{N}_2\text{O}$ flame, respectively. The peaks are labelled with the vibrational quantum numbers of the states participating and the asymmetric broadening of the peaks is due to rotational transitions. Vibrational temperatures are obtained from computing the ratio of the relative Q branch vibrational intensities

$$\frac{I(\nu+1, \nu)}{I(1 \rightarrow 0)}$$

and comparing these ratios with those obtained using the computer program (Appendix) with the appropriate experimental parameters. The vibrational temperatures obtained are $T = 1180, 1680, \text{ and } 2180^\circ\text{K}$ for Figures 7, 8, and 9, respectively.

V. DISCUSSION

Clearly, at low temperature pure rotational Raman spectra give more accurate temperature measurements since excited vibrational state populations are small. However, as the temperature increases the excited vibrational population grows making the ro-vib spectra more attractive. At the same time, rotational transitions within vibrational excited states complicate the pure rotational spectra resulting in a decrease in the accuracy. It has been suggested⁶ that below temperatures of $\sim 2000^\circ\text{K}$ pure rotational Raman is more accurate, provided rotational spectra of other molecules do not mask the spectra of interest. Above this temperature ro-vib Raman spectra are more accurate.

⁶Michael C. Drake, Chamnong Asawaroenghai, and Gerd M. Rosenblatt, "Temperature from Rotational and Vibrational Raman Scattering: Effects of Vibrational-Rotational Interactions and other Corrections", Div. of Phys. Chem. ACS, Washington Meeting, Sept 1979.

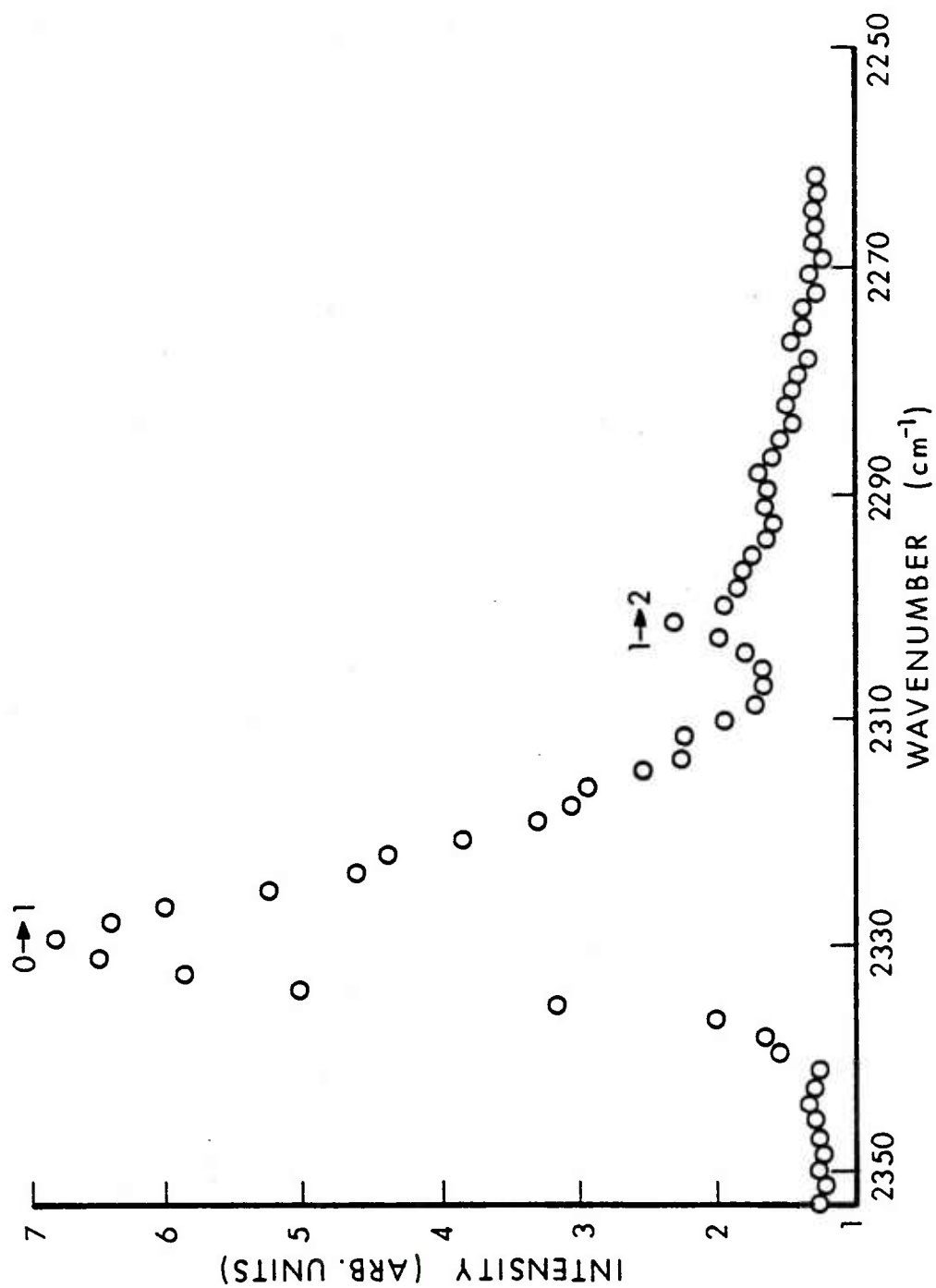


Figure 7. Stokes Q branch Raman rotational-vibrational spectrum for N₂ in a rich CH₄/air flame on a small slot burner.

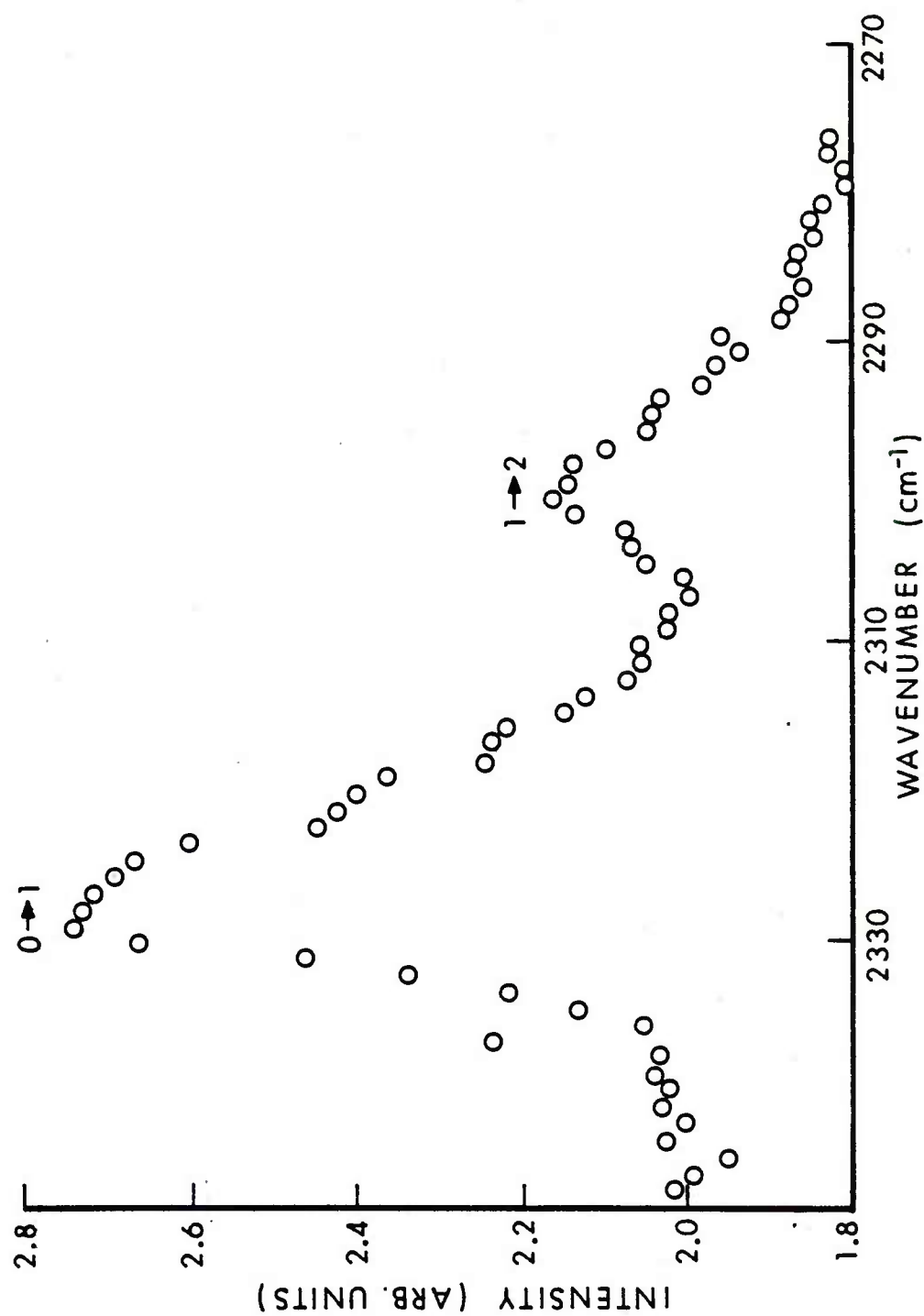


Figure 8. Stokes Q branch Raman rotational-vibrational spectrum for N₂ in a near stoichiometric CH₄/air flame on a small slot burner.

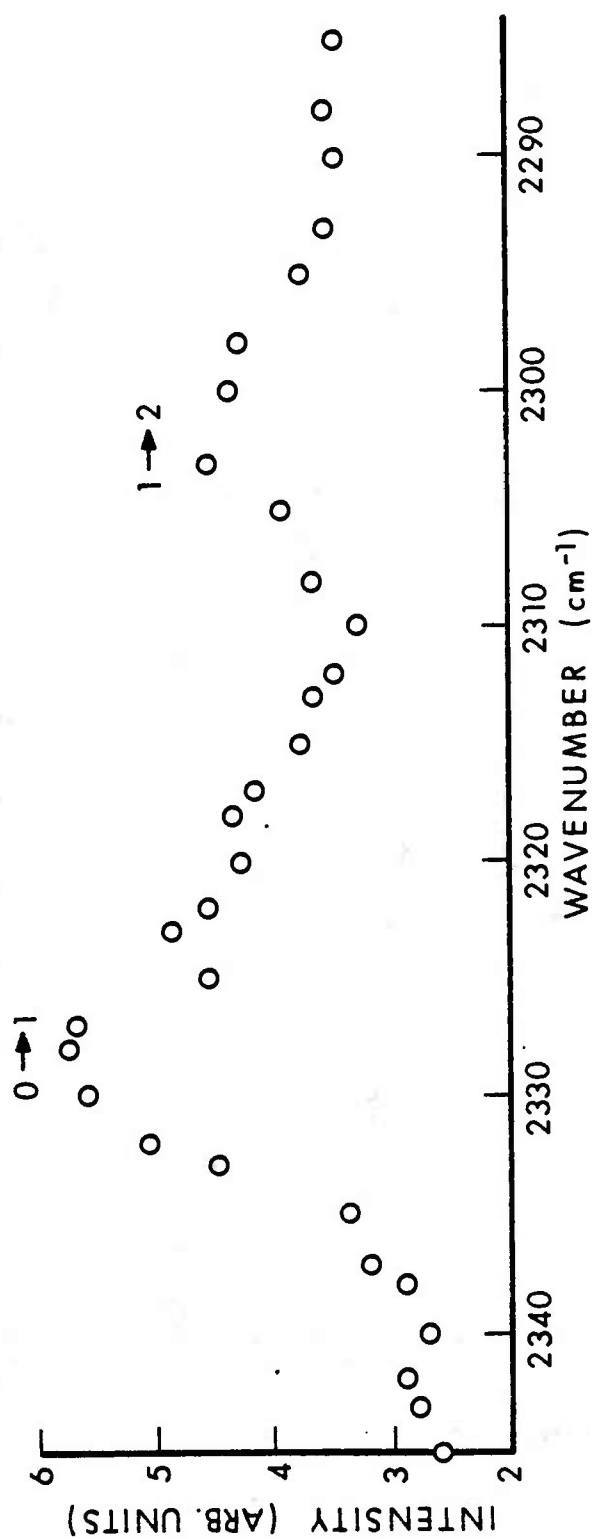


Figure 9. Stokes Q branch Raman rotational-vibrational spectrum for N₂ in a near stoichiometric CH₄/N₂O flame on a small slot burner.

Many investigators⁵⁻¹⁵ have utilized Raman spectroscopy for flame temperature measurements; temperatures obtained for a near stoichiometric atmospheric pressure CH₄/air flame have ranged from 1500 to 2000°K.^{5,7,9,15} We obtain a temperature of 1680°K from ro-vib Raman spectra. Adiabatic flame temperature calculations from a version of the NASA-Lewis thermochemical code¹⁶ give 2169¹⁵ and 2166°K for CH₄/air stoichiometric mixtures at atmospheric pressure. The experimental values have fallen below these values and this is attributed either to the effects of heat loss to the burner head or to cooling from the entrainment of air into the flame.

Both pure rotational and ro-vib Raman spectra were used to obtain temperatures of 1830 and 2180°K, respectively for near stoichiometric mixtures of CH₄/N₂O burning at atmospheric pressure. The lower temperature obtained by pure rotational Raman scattering is attributed to the influence of rotational scattering from vibrationally excited molecules. Drake, et al.,³ calculate that this effect raises the temperature by 8%

⁷ Alan C. Eckbreth, "Laser Raman Gas Thermometry", AIAA Paper No. 74-1144 Oct. 1974.

⁸ M. Lapp, L. M. Goldman, and C. M. Penney, "Raman Scattering from Flames", *Science*, 175, 1112-1115 (1972).

⁹ S. M. Schoenung and R. E. Mitchell, "Comparison of Raman and Thermocouple Temperature Measurements in Flames", *Combustion and Flame*, 35 207-211 (1979).

¹⁰ W. Stricker, "Local Temperature Measurements in Flames by Laser Raman Spectroscopy", *Combustion and Flame*, 27, 133-136 (1976).

¹¹ M. Lapp and C. M. Penney, eds., *Laser Raman Gas Diagnostics*, (Plenum Press, New York, 1973).

¹² D. P. Aeschliman, J. C. Cummings, and R. A. Hill, "Raman Spectroscopic Study of a Laminar Hydrogen Diffusion Flame in Air", *J. Quant. Spectrosc. Radiat. Transfer*, 3, 293-307 (1979).

¹³ William M. Arden, Thomas B. Hirschfeld, Stanley M. Klainer, and William A. Mueller, "Studies of Gaseous Flame Combustion Products by Raman Spectroscopy", *Appl. Spectrosc.* 28, 554-557 (1974).

¹⁴ A. A. Boiarski, R. H. Barner, and J. F. Kircher, "Flame Measurements Utilizing Raman Scattering", *Combustion and Flame*, 32, 111-114 (1978).

¹⁵ James H. Bechtel, "Temperature Measurements of the Hydroxyl Radical and Molecular Nitrogen in Premixed Laminar Flames by Laser Techniques", *Applied Optics* 18, 2100 (1979).

¹⁶ R. A. Svehla and B. J. McBride, NASA TND-7056 (1973).

for N₂ at 2000°K using a 2.6 cm⁻¹ slit width. Our slit width is similar. For comparison purposes, the temperature has also been measured by line reversal using the OH present in the flame. A temperature of 2211 ± 45K was obtained. A 3" diameter sintered bronze flat flame burner has also been used to obtain the flame temperature for a near stoichiometric CH₄/air atmospheric pressure flame.¹⁷ Initial results gave temperatures around 2100°K; more recent results indicate a temperature of 2200°K. Line reversal using OH was also used with this burner and a temperature of 2194 ± 25K obtained. The calculated adiabatic flame temperature for this flame was much higher, 2922°K.¹⁸ Three different experimental techniques suggest the flame temperature is ~ 2200°K. Cooling by the burner head and/or equilibrium conditions not being reached may account for the substantial discrepancy between the adiabatic flame temperature calculation and experimental results.

VI. SUMMARY

Extracting a temperature from both pure rotational and ro-vib Q branch Raman spectra of molecular nitrogen in a flame has been accomplished. A flame temperature for a CH₄/N₂O flame has been measured. Error limits have been presented for rotational Raman temperature data. Error limits for ro-vib Raman temperature data will be addressed elsewhere¹⁹ but are usually less than ± 50K for clean flames.

¹⁷William R. Anderson, "Laser Excited Fluorescence Measurement of OH Rotational Temperatures in a CH₄/N₂O Flame", Eastern Sectional Meeting, Combustion Institute, Atlanta, Georgia, Nov 1979.

¹⁸R. A. Hill, A. J. Mulac, D. P. Aeschliman, and W. L. Flower, "Temperatures from Rotational-Vibrational Raman Q Branches", *J. Quant. Spectrosc. Radiat. Transfer*, 21, 213-220 (1979).

¹⁹R. A. Beyer and J. A. Vanderhoff, "Raman Spectroscopy of Premixed CH₄/N₂O Flames", BRL report in preparation.

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APPENDIX

This Appendix contains the computer program used to generate the Stokes Q branch ro-vib Raman spectrum for N₂ as a function of temperature. Four vibrational levels and 70 rotational levels are included.

MOLECULAR AND EXPERIMENTAL PARAMETERS

<u>Symbol in Text</u>	<u>Symbol in Program</u>	<u>Value</u>
W_e	WE	2359.61 cm ⁻¹
$W_e X_e$	WEXE	14.46 cm ⁻¹
$W_e Y_e$	WEYE	0.00751 cm ⁻¹
B_o	BE	1.9986
α_e	AE	0.01803
v	I	0-4
J	J	0-70
ν_o	WO	20491.81 cm ⁻¹
-	DEL (slit width triangular function where DEL = fwhm)	6 cm ⁻¹
C	C	1X10 ⁻¹⁵

This program calculates the 0-1, 1-2, 2-3, and 3-4 ro-vib Raman Q branch spectrum and displays the plot on a TV monitor. A light pen is used to extract the peak values.

PROGRAM LISTING

```

C   DG is the Raman shift and WR is the Raman
C   frequency for the ro-vib Raman line positions.
C   S is the intensity for the ro-vib Raman
C   Stokes Q branch transitions. ISUM is the
C   intensity convoluted with a monochromator
C   slit function
C   DIMENSION WR (6,80), S(6,80), ISUM(1500)
C   EXTERNAL PEN
C   CALL INTSET ('324, 4, ID, PEN)
```

```

CALL DSPLPN (1)
REAL I, J
C   ENTER VARIABLES, TEMPERATURE AND
    THE MONOCHROMATOR SLIT FUNCTION
TYPE 100
100  FORMAT (3X, 'ENTER T', 10X, 'ENTER DEL'/)
    ACCEPT 11D, T, DEL
110  FORMAT (2F10.0)
    HCK = 1.44
    WO = 20491.81
    BE = 1.9986
    WEXE = 14.456
    WEYE = .00751
    AE = .01803
    WE = 2359.61
    C = 1E-15
    G = 1.0
    K = 1
    MIN = 32000
    MAX = 0
    H = DEL/6.
C   Upper and lower limits on frequency for
C   computation of synthetic spectra.
    WL = WO - (WE - WEXE) - DEL
    WU = WO - (5*WEXE + DEL)
    NNX = 4095/NPTS
    W = WL
C   Rotational and vibrational partition functions
    QR = T/(2*HCK*BE)
    QV = 1./(1-EXP((-HCK/T)*(WE - WEXE + .75 WEYE)))
    PRINT 120
120  FORMAT (3X 'WAVENUM', 13X, 'STOKES Q INTENSITY', 6X, 'V', 9X 'J'/)
C   Calculation of the ro-vib Q branch
C   Stokes Raman line positions and intensities
    DO 130 II = 1,5
    DO 140 JJ = 1,71
    I = II - 1
    J = JJ - 1
    DG = WE - 2*WEXE* (I + 1) + WEYE* (3*I*I* + 6 + 13/4) - AE*J*(J+1)
    WR (II, JJ) = WO - DG
    F = INT (J/2) - J/2
    IF (F.LT.0) G = .5
    S(II, JJ) = (G/QR*QV)* (2*J + 1)*(I+1)*(WR(II,JJ)**4)*C*EXP (- (HCK/T)*
    (WE*(I + .5) + WEXE *((I + .5)**2) + WEYE*((I + .5)**3) + (BE -AE/2)*
    J*(J+1) - AE*I*J*(J+1)))
    PRINT 150, WR(II,JJ), S(II,JJ), I, J
150  FORMAT (1X, E13.7, 10X, E13.5, 7X, F5.1, 5X, F5.1)
140  CONTINUE
130  CONTINUE
    PRINT 160

```

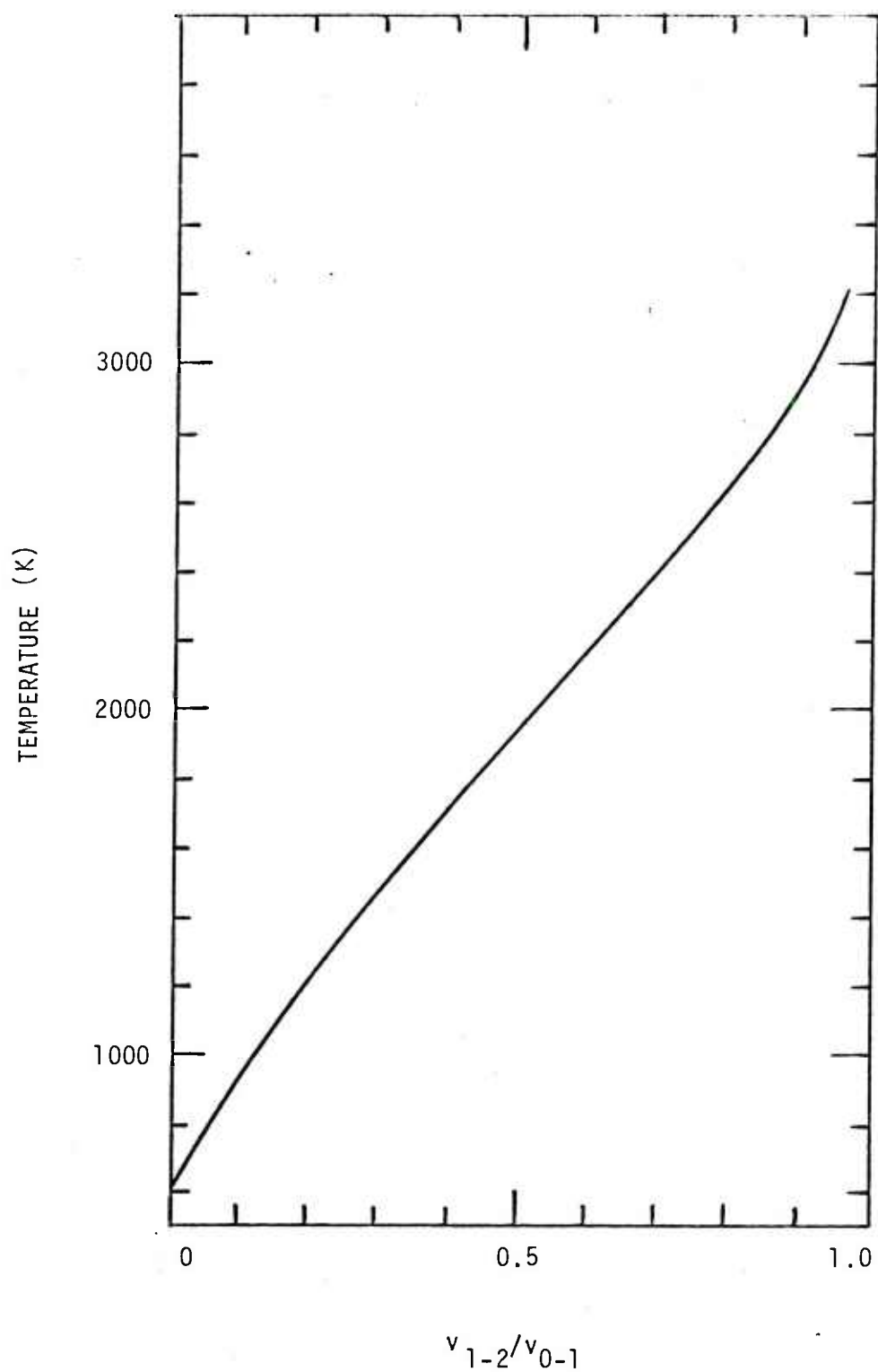
```

160  FORMAT (3X, 'MONWAVE' 13X 'SLIT INT INTENSITY'/)
C    CONVOLUTION OF INTENSITIES WITH
    MONOCHROMATOR SLIT FUNCTION
170  CONTINUE
    SUM = 0.
    SW = 0.
    DO 180 II = 1,5
    DO 190 JJ = 1,75
    I = II - 1
    J = JJ - 1
    IF (WR(II,JJ).GE.W-DEL.AND.WR(II,JJ).LE.W) SW = (WR(II,JJ) + DEL - W)*
    S(II,JJ)/DEL
    IF(WR(II,JJ).GT.W.AND.WR(II,JJ).LE.W + DEL) SW = (W + DEL - WR(II,JJ))*
    S(II,JJ)/DEL
    SUM = SUM + SW
190  CONTINUE
180  CONTINUE
    PRINT 200, W, SUM
200  FORMAT(IX,EI3.7, 10X, EI3.5)
    IF (W.GT.WU)GO TO 230
    W = W + H
    ISUM (K) = SUM
    K = K + 1
    GO TO 170
C    SCALING THE DISPLAY
    DO 210, M = 1, NPTS
    IF (ISUM(M).LT.MIN) MIN = ISUM(M)
    IF (ISUM(M).GT.MAX) MAX = ISUM(M)
210  CONTINUE
    IDIFF = MAX - MIN
    IYSCALE = IDIFF/1023
    DO 220 M = 1, NPTS
    ISUM(M) = (ISUM(M) - MIN)/IYSCALE
220  CONTINUE
230  CALL DSPMO1 (NPTS, ISUM, NNK, 0)
    GO TO 230
    CALL EXIT
    END
    SUBROUTINE PEN (ID)
    CALL READ (MOD, IX, IY)
    IF (MOD.EQ.I) TYPE 100, IX, IY
    FORMAT (2I1D)
    IF (MOD.EQ.1) CALL WAIT (2.)
    END

```

TABLE 1. RATIO OF 0-1 TO 1-2 VIBRATIONAL PEAKS AS A FUNCTION
OF TEMPERATURE

<u>Temperature</u> <u>Kelvin</u>	<u>DEL</u> <u>cm-1</u>	<u>V1-2</u> <u>V0-1</u>
1000	6	0.078
1200	6	0.142
1400	6	0.218
1600	6	0.301
1800	6	0.389
2000	6	0.478
2200	6	0.565
2300	6	0.607
2400	6	0.647
2500	6	0.688
2600	6	0.728
2800	6	0.804
3000	6	0.816



Temperature versus the ratio of the first two Raman rotational-vibrational peaks of N₂, from computer-generated Raman spectra.

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